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Lamellar to Onion Transitions with Increasing Temperature under Shear Flow in a Nonionic Surfactant/Water System Studied by Rheo-SAXS

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Introduction

In the past 15 years, much attention has been paid to the effects of shear flow on the structure of the lyotropic phase. Among them, the lamellar phase has become of interest because the shear induced state is sometimes not simply related to an existing equilibrium. After the pioneering study of Roux et al., who have found transition from the lamellar phase to the onion phase where multilamellar vesicles are close-packed, various types of shear effects have been reported [1]. In our previous study [2, 3], we have measured small-angle neutron scattering on the lamellar phase of a nonionic surfactant $C_{16}H_{33}(OC_2H_4)_7$/water system at 70°C under shear flow in the range of shear rate 0.3 - 30 s^{-1}. We have found that the lamellar spacing decreases discontinuously with increasing shear rate and takes a minimum at around 1 s^{-1}.

In the present study, simultaneous SAXS/rheology measurements (rheo-SAXS) have been performed as a function of temperature on the same system.

Experimental

A rheometer AR550 (TA Instruments) is modified for rheo-SAXS experiments. Details of the cell have been reported previously [4]. Measurements were performed on the beamline 15A. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.015 to 0.25 $Å^{-1}$.

Results

Figure 1 shows temperature dependence of the shear stress and 2-D SAXS patterns for the lamellar phase of a $C_{16}E_7$/water system (48 wt%) or the shear rate of 3 s^{-1}. As the temperature increases from 67°C to 69°C, the shear stress (or viscosity) increases more than one decade. At the same time, the orientation of lamellae disappears rapidly as can be seen from the 2-D SAXS patterns. We have also performed simultaneous measurements of small-angle light scattering (SALS) and shear stress for the same system under the same condition. A so-called four-lobe pattern has been observed accompanied by the rapid increase in the shear stress. These results strongly suggest formation of onions with increasing temperature.

From the measurements for different concentrations, it has been found that the lamellar/onion transition occurs only in a narrow concentration range (48-54 wt% at 3 s^{-1}) and that the transition temperature increases steeply with increasing concentration.

The onion to lamellar transition with increasing temperature under shear flow has been reported in a few surfactant systems, which is explained in terms of increase (less negative) in the saddle-spray modulus of bilayers with the temperature elevation [5]. Our findings are apparently controversial with these results. However, our results can be explained by taking into account the "effective" volume fraction of water layers at rest.

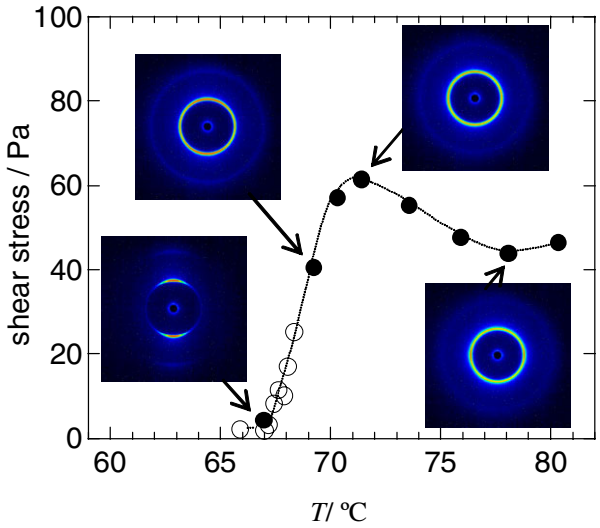

Fig. 1 Temperature dependence of the shear stress (different symbols indicate different runs) and 2-D SAXS patterns for the lamellar phase of a $C_{16}E_7$/water system (48 wt%) at 3 s^{-1}. The flow direction is horizontal.

References

[1] W. Richtreing, *Curr. Opin. Colloid Interface Sci.* **6**, 446 (2001).
[2] T. Kato, K. Minewaki, Y. Kawabata, M. Imai, and Y, Takahashi, *Langmuir* **20**, 3504 (2004).
[3] K. Miyazaki, Y. Kosaka, Y. Kawabata, S. Komura, and T. Kato, *J. Appl. Cryst.* **40**, s332 (2007).
[4] T. Kato, K. Miyazaki, Y. Kosaka, and Y. Kawabata, *PF Activity Report 2005,* **23**, Part B (2006).
[5] T. D. Le, U. Olsson, K. Mortensen, J. Zipfel, and W. Richtering, *Langmuir* ***17***, 999 (2001).

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